

# Mass Spectrometry Forum

## Space Charge in Mass Spectrometry

This column discusses the space charge effect, which is rooted in the physics of interaction between charged particles, with direct implications in MS instrument design and consequences in their performance.

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**M**anagement: “Sensitivity seems worse than usual in this analysis, Ken.”

Hapless Ken: “We’re having some space charge effects in the source that are causing beam defocusing. I’ve called the manufacturer and they are looking into it.”

The hypothetical exchange quoted above illustrates three important maxims in mass spectrometry (MS). First, “management” always seems to expect maximum sensitivity at all times, in all analyses, no matter how dirty the sample, no matter how many samples there are, no matter how little time is allowed for instrument maintenance, and no matter that the instrument might be many years past its analytical prime. Second, high technology phrases such as “space charge” or “beam defocusing” are useful and integral parts of explanations, even if perhaps not everyone knows what these terms mean, and whether or not they might be appropriate for the situation. Third, always look to the manufacturer to resolve promptly any and all issues — even issues that are not their responsibility —



**Kenneth L. Busch** likes to think of space charge as traffic congestion for ions. Sometimes you can widen the road, and sometimes you can change the speed limit, but you can't make the vehicles any smaller. Since you can squeeze more than one charge into a single vehicle, you might consider HCV (high charge vehicles), but then you discover that the highly

charged vehicles demand more space around them, so you don't gain as much as you think. Ions don't telecommute, but they do play statistics. Ion statistics is a topic for a future column. Opinions expressed in this article are those of the author and not those of the National Science Foundation. Thanks to Marc Engel for suggesting the topic for this column. Contact the author at buschken@hotmail.com.

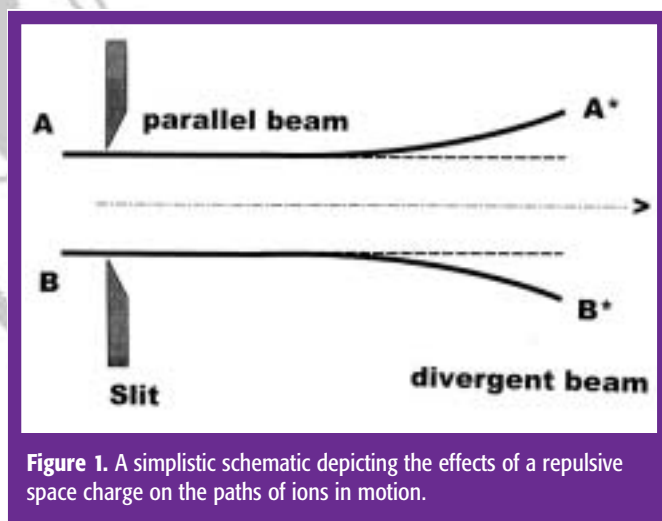


Figure 1. A simplistic schematic depicting the effects of a repulsive space charge on the paths of ions in motion.

because we all know that those folks have plenty of spare time, and not enough to do to keep busy.

To prepare for your own hypothetical exchange with management, we address in this column the definition and importance of space charge. The space charge effect is rooted in the physics of interaction between charged particles, with direct applications in instrument design for various types of mass spectrometers, and consequences in their analytical performance. Recently, space charge effects have been studied specifically in Fourier-transform (FT) and ion-trap mass spectrometers, and in miniaturized electrospray ionization (ESI) sources. Furthermore, consideration of space charge and its effects is a recurring topic in accelerator MS. Finally, scientists involved in the development of spacecraft mass spectrometers, constrained by space and power limits, have long been acutely aware of the limitations imposed by space charge. We earth-bound types will limit ourselves to terrestrial applications.

### The Significance of Space Charge

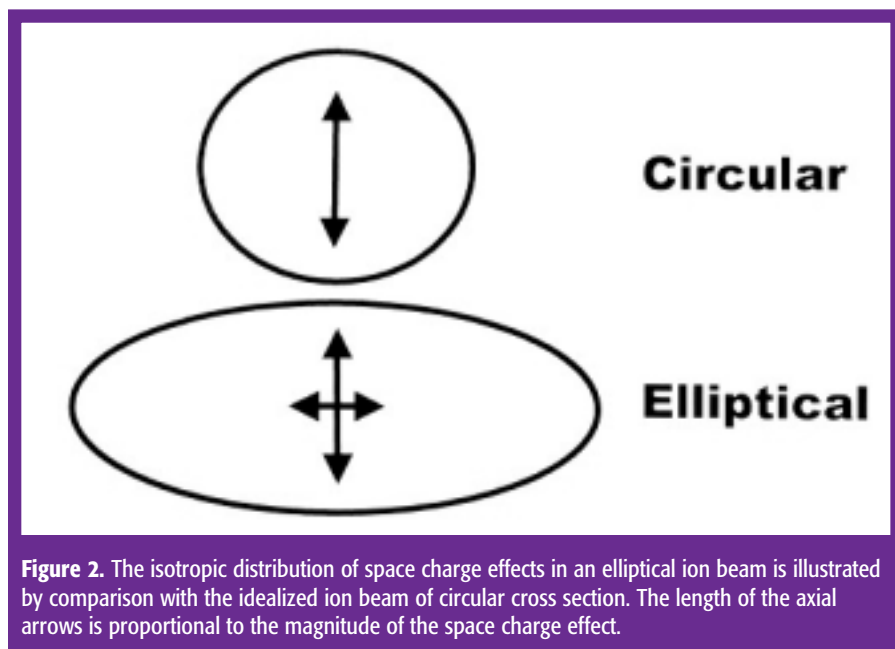
In the simplest sense, space charge effects are a consequence

of the mutual repulsion between particles of like charge. Space charge is a consequence of Coulomb's law, which quantifies the force ( $F$ ) between two point charges ( $q$  and  $q'$ ) separated by a distance  $r$  as:

$$F = k(qq'/r^2)$$

where  $k$  is a proportionality constant that depends upon the units chosen for the other variables in the equation. Note that Coulomb's law describes both the force of attraction between particles of opposite charges, and the force of repulsion between like charges. In a mass spectrometer, the particles (ions) are usually of like charges, and the intervening medium (a vacuum) does not mediate the force significantly. However, even at atmospheric pressure, the correction required is relatively small and can be described mathematically. Within ion sources and beam mass spectrometers, the effects of space charge are manifest in moving charges, but in two distinct venues. In an ion source (and before any mass separation in the beam instrument), ions of all different masses are coincident in space. Space charge effects are imposed on a collection of ions of different masses and different energies. After the mass separation, the ions are dispersed in space, and the effects of space charge are both simplified and concomitantly reduced. In mass analyzers such as FT and ion-trap mass spectrometers, the consequences of space charge play out within the collection of ions of all masses stored in a constrained area in the mass analyzer. Space charge effects can be considered separately for each mass-selected packet of ions. In both cases, space charge affects both mass measurement accuracy and sensitivity, and emphasizes the need for its comprehension.

A conceptual diagram of two charged particles moving in parallel paths is shown in Figure 1. At sufficiently small scale, this will suffice to describe the movement of an ion beam whether within an ion source, through a magnetic analyzer, or following a constrained circular orbit



**Figure 2.** The isotropic distribution of space charge effects in an elliptical ion beam is illustrated by comparison with the idealized ion beam of circular cross section. The length of the axial arrows is proportional to the magnitude of the space charge effect.

within an ion-trap or FT mass spectrometer. In the absence of any interaction between the ions (a consequence of a sufficiently large distance between the two ions), the paths of the ions will continue to be parallel. If the distance is small, or if the ions are more highly charged (still considering each as a point source), then space charge will cause a divergence from the parallel paths, as shown.

Multiple ions moving together in the same direction constitute an ion beam. The mathematical model of space charge is developed more fully for ion beams with either circular (the ideal case) or elliptical (the usual case) cross sections. The development of the full mathematical model is important in beam mass spectrometers because focusing elements are often isotropic, operating in one axis or the other, but not both equally or simultaneously. An image on an ion beam derived from the detector's perspective is shown in Figure 2. Space charge changes the effect of an external field (such as a focusing plate or lens) on the ion beam of an external field, either reducing or increasing any focusing action otherwise achieved. Rigorous derivation shows that the space charge effect increases with the amount of ion current carried by the beam (more ions result in more space charge), and is inversely proportional to the ion veloc-

ity (slower ions are more perturbed in their trajectories than faster moving ions). In an ion beam accelerated through a constant potential, the slower moving ions will be the higher mass ions. An immediate deduction is that because faster moving ions are affected less, beam instruments with higher accelerating potentials (source operating voltages) should exhibit higher instrument sensitivities.

Given an accurate mathematical model of the expected interactions between ions in beams of various profiles, the effects of space charge in an ion optical device can be calculated by iteration and summation of the affected individual ion trajectories. For example, the BEAM-TRACE program (1) provides a trajectory distribution through a given ion optical element for a kilovolt ion beam subject to space charge effects. Use of similar programs supports the design of mass spectrometer ion sources and analyzers, and also can be used to track the consequences of space charge in ion storage mass analyzers. Space charge is a dynamic effect, and so the model presented by a calculational program must be integrated over an appropriate time of ion residence in the device.

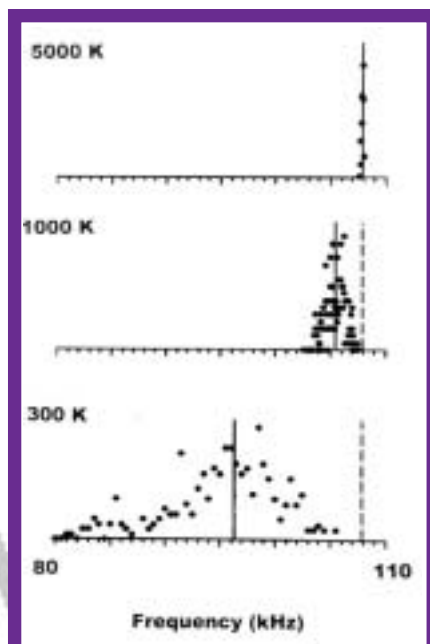
### Consequences in Various MS Application Areas

The remainder of this column

explores the consequences of space charge in three different areas of application in MS. The first of these is inductively coupled plasma mass spectrometry (ICP-MS), in which the space charge derived from a surfeit of an easily ionized matrix constituent reduces sensitivity. Because ICP-MS is used for ultratrace elemental detection in a complex mixture of elements, such deleterious effects undermine the usefulness of such analyses. The second area is the effect of space charge on accurate mass measurements obtained in FT-MS, used for accurate mass measurements of biological ions. Space charge operates limits the accuracy of mass measurement in FT mass spectrometers. The third area discussed is the effect of space charge in ion-trap mass spectrometers, where the space charge effect is convoluted with the effects of repeated collisions between the ions and the gas (usually helium) present in the trap at a pressure of about  $10^{-3}$  torr. Space charge affects the basic ability to store ions efficiently within the trap. These widely diverse applications areas underscore the importance of a fundamental understanding of space charge and its effects.

Stewart and Olesik (2) tracked specific effects of space charge on the transport of ions from the inductively coupled plasma into a mass analyzer using a vertically oriented piezoelectric device to generate consistently small droplets subsequently introduced into the plasma. Assume that  $x$  is the direction of movement of ions from the plasma into the mass analyzer (axial direction), and  $r$  is the radial distribution of ions around that central axis. Space charge operates anisotropically, and so would be expected to influence ion movement in either direction. However, different axial and radial effects could be deduced. The radial effects resulted in an ion transmission loss, while the axial effects of space charge are convoluted within different ion velocities for ions of different mass. This difference in velocities is directly evident in separate arrivals of ion clouds for ions of different masses. Additionally, howev-

er, the generation of a bimodal arrival time distribution for a lower mass analyte ion was ascribed to a space charge effect induced by a perturbing cloud of matrix ions. The authors drew detailed conclusions regarding the site of final droplet desolvation and point of maximum space charge interaction. Radial effects of space charge were apparent in changes in analyte ion response proportional to the intensity of the matrix ion signal.



**Figure 3.** Results of a numerical simulation for shifts in frequency for ions held within a collision gas characterized by three temperatures. The mean predicted frequency is shown by the solid line; the unperturbed frequency is shown by the dashed line. The figure is adapted from reference 4.

The ability of FT mass spectrometers to provide high accuracy mass measurements is a consequence of the ability of the instrument to measure accurately the frequency of orbits of ions trapped in the cyclotron cell. With a limited number of ions in paths unperturbed by space charge, the accuracy of mass determination is electronic noise-limited. More ions would seem to be the solution, because more ions lead to more measured signal, and therefore an increase in accuracy. But as the number of ions increases, accuracy is degraded because the ions start

to interact with each other through a space charge effect. Accuracy is maximized when there are (depending upon a number of parameters) approximately from  $10^3$  to  $10^4$  ions trapped within the cell. For an internal mass calibration experiment, this population of ions contains ions from the calibrant itself. As a result, external calibration methods have been developed to maximize the number of ions from the sample itself. However, the internal calibration method remains the method of choice for highest accuracy. As a consequence, the calibration function usually includes a term that provides a first order correction for space charge effects. Masselon and colleagues (3) completed a systematic study of the errors associated with the mass measurements so determined. The magnitude of the error is related to the number of ions of each particular mass. Each different ion cloud experiences a slightly different space charge effect, and a global correction that simply accounts for the total number of ions is limited in accuracy. A modified calibration equation was proposed that reflects the fact that ion clouds that contain a higher number of ions are more affected by the space charge, and the measured masses of such ions need to be corrected appropriately.

The third application area presents the consequences of space charge in an ion-trap mass spectrometer. Ion-trap instruments are attractive in their relatively high performance coupled with a small footprint and a lower relative cost. The ion trap itself is physically small, portending the importance of space charge and the attendant limit on the number of ions that can be stored in the trap at any one time. In addition to space charge effects, the ion trap operates at a pressure of about  $10^{-3}$  torr helium, in contrast to an FT mass spectrometer maintained at  $10^{-8}$  torr. Parks and Szöke (4) have described a comprehensive simulation for the motions of ions held in an ion trap that takes into account collisions between the stored ions and the helium gas, along with space charge effects. Space charge interaction between ions in a

coherent cloud tends to expand the cloud (that is, the radius of the orbit is increased), as does collision. The assumptions of the simulation require that the charge density be less than about  $10^8$  ions/cm<sup>3</sup>. The simulations show that the space charge effects are most significant when the temperature of the cloud is lower; that is, when collisional effects themselves are less significant. The temperature reflects the collection of ion velocities within the cloud, which is assumed to be in equilibrium with the temperature of the helium gas. For any given ion cloud that orbits within the trap at a given frequency, the effect of space charge is to cause a decrease in the mean observed frequency and a broadening of the width of the frequency signal. This effect is more noticeable at lower temperatures (slower moving ions). Figure 3 (redrawn from the original figure of Parks and Szöke) illustrates this effect for ion ensembles containing 400 ions at three temperatures. The solid line is

the mean frequency; the dotted line is the unperturbed frequency. The effect at lower temperatures is significant, shifting the mean and broadening the distribution. The consequence of space charge in the efficiency of similar frequencies introduced to the trap to selectively remove or excite specific ions is clear.

### Conclusion

Space charge between two ions held motionless in a vacuum can be exactly described mathematically. A more complex mathematical model applies to ions in motion, as is always the case in mass spectrometry. Complexity also ensues when the number of ions increases, when numbers of ions of different masses are substantially different, and when the effects of space charge are convoluted with collisions that can act to excite or relax the ions. Even under such complicating circumstances, numerical simulations allow the detailed effects to be predicted, and specific

experiments can be designed to delineate these effects. With increasing interest in miniature and portable mass spectrometers, the importance of space charge effects in the design and operation of the ion source and the mass analyzer will be magnified.

### References

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